Characterization of Catalyst Materials for Production of Aerospace Fuels

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Abstract

Due to environmental, economic, and security issues, there is a greater need for cleaner alternative fuels. There will undoubtedly be a shift from crude oil to non-petroleum sources as a feedstock for aviation (and other transportation) fuels. Additionally, efforts are concentrated on reducing costs coupled with fuel production from non-conventional sources. One solution to this issue is Fischer-Tropsch gas-to-liquid technology. Fischer-Tropsch processing of synthesis gas (CO/H_2) produces a complex product stream of paraffins, olefins, and oxygenated compounds such as alcohols and aldehydes. The Fisher-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur or aromatic compounds. This process is most commonly catalyzed by heterogeneous (in this case, silver and platinum) catalysts composed of cobalt supported on alumina or unsupported alloyed iron powders. Physisorption, chemisorptions, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) are described to better understand the potential performance of Fischer-Tropsch cobalt on alumina catalysts promoted with silver and platinum. The overall goal is to preferentially produce C8 to C18 paraffin compounds for use as aerospace fuels. Progress towards this goal will eventually be updated and achieved by a more thorough understanding of the characterization of catalyst materials. This work was supported by NASA's Subsonic Fixed Wing and In-situ Resource Utilization projects.

Nomenclature

BET   Brunauer, Emmett, and Teller surface area analysis method (physisorption)

C constant related to the energy of adsorption

CO   carbon monoxide

CO_2 carbon dioxide

CSTR   continuously-stirred tank reactor

EDS   energy dispersive spectroscopy

FT(S)   Fischer-Tropsch (synthesis)

GRC   NASA Glenn Research Center

GTL   gas-to-liquid

P pressure

P_0 vapor pressure of liquefied gas at the adsorbing temperature

SEM   scanning electron microscopy

TCD   thermal conductivity detector

TPR   temperature-programmed reduction (chemisorption analysis method)

V_a STP volume of gas adsorbed at pressure P

V_m STP volume of gas needed to form an adsorbed monolayer

Introduction

For much of the last 2 centuries, fossil fuels, most notably petroleum, have facilitated the rapid growth and development of the modern transportation system used throughout the world today. At the conclusion of the twentieth century, the reality of society's over-reliance and misuse of non-renewable resources became evident. As a result, throughout scientific and political arenas, new and affordable renewable energies have become key to the future preservation of an energy-intensive society. Space and aviation vehicles require high energy density liquids for propulsion (and power), thus differentiating them from conventional "green" energies available for terrestrial and marine propulsions (electric, nuclear, etc.). At the NASA Glenn Research Center (GRC), research is focused on alternative fuels derived from Fischer-Tropsch synthesis (FTS) and other gas-to-liquid (GTL)

processes for aerospace propulsions. There are many objectives branching from FT research, including analysis of specific promoters for particular fuel compositions, optimization of the synthesis of FT catalysts, and end product improvement to enable the goal of reduced reliance on non-renewable sources for aerospace fuels.

The FTS reaction can be described as a series of chemical reactions used to convert synthesis gas (CO/H_2) into useful hydrocarbon products. The process generally includes the following two highly exothermic reactions:

$$(2n+1)H_2 + nCO => C_nH_{2n+2} + nH_2O \qquad (1)$$

$$2nH_2 + nCO => C_nH_{2n} + nH_2O \qquad (2)$$
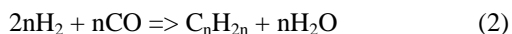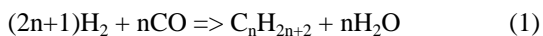
The hydrocarbon product stream is a very complex mixture, containing paraffins, olefins, and oxygenated compounds such as alcohols (Ref. 1). Fischer-Tropsch synthesis is an essential component of GTL technologies and is a noteworthy alternative fuel source, since the resultant alkanes and alkenes can be converted into useful aviation fuel ($C_8 - C_{18}$ hydrocarbon chains). There are several key advantages to FT-derived fuels. Since products do not contain sulfurs, heavy metals, or aromatics, emissions are greatly reduced; FT fuels are much more environmentally friendly than those derived from petroleum (Ref. 2).

FTS is based on a radical mechanism. In order for the FT reaction to proceed, a metallic catalyst must be used to facilitate the reaction between CO and H_2. The reaction is a surface-catalyzed polymerization reaction that links $-CH_2$ monomers from CO and H_2 (Ref. 3). The overall performance of the reaction is based on many factors, but most importantly the synthesis gas and catalyst composition, and the operating temperature. For the GTL processes, the feed gas is most commonly obtained from methane, but can be acquired from coal and crude oil via steam reforming or partial oxidation or through biomass derivatives (Refs. 4 and 5).

As a result of decades of research, it is now known that the most active metals for FT synthesis are nickel (Ni), ruthenium (Ru), cobalt (Co), and iron (Fe) (Ref. 6). However, the most common metals used for commercial applications of FT synthesis contain Co and Fe since they are less expensive than Ru and Ni, which predominately produces methane. Typical FT synthesis is catalyzed by cobalt on alumina (Al_2O_3), which may include additional transition metal promoters (ex. Pt, Ag, Pd, Mn, etc.), or unsupported alloyed iron powders. The main difference between the iron and cobalt catalysts involves the formation of oxygen-containing products. When reacted, the oxygen from the synthesis gas is converted to water with cobalt catalysts and CO_2 with iron (Ref. 7). Since cobalt does not have significant water-gas-shift (WGS) activity (iron has considerable WGS activity), the synthesis gas ratio of H_2:CO must be higher than 2:1. This ratio is typical of syn-gas derived from natural gas (CH_4). As natural gas availability is currently the main driving force behind FT synthesis, cobalt

catalysts are primarily used. Cobalt is also more rugged and can be used for multiple GTL conversions; which further reduces the cost of feedstock production. Moreover, Co has a much lower yield of oxygen-containing products including ketones, alcohols, and aldehydes which further promotes the use of this metal (Ref. 8).

Currently, there are two standard sets of FT operating conditions, high temperature and low temperature. Typically, for high temperature (300 to 350 °C) conditions, the alloyed iron catalysts are used for the production of low molecular weight olefins, whereas the low temperature (200 to 240 °C) reactions use cobalt catalysts to promote the production of high molecular weight saturated paraffins or waxes (Ref. 9). At GRC, cobalt FT catalysts are used in the Alternative Fuels Research Laboratory in three continuously-stirred tank reactors (CSTRs) for the production of FT hydrocarbons, one for Fe and two for Co.

Before catalysts are tested or run in FT reactors, they are typically characterized by various analytical techniques: scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS); temperature programmed reduction (TPR, or chemisorption); and Brunauer, Emmett, and Teller surface area analysis (BET, or physisorption). The main goal of characterization is to indicate promising FT synthesis catalysts that promote products within the transportation fuel and additives range ($C_8 - C_{18}$). Additionally, the use of transition metals as promoters is used to enhance the catalytic properties of the FT catalysts, most commonly ruthenium, platinum, and rhenium. Promoters are very valuable to the FT process and have been shown to increase catalytic activity and the reducibility of cobalt oxide, improve mechanical properties, and stabilize high surface area catalysts (Refs. 10 and 11). Promoter alternatives include silver, nickel, palladium, and manganese. However silver and manganese are especially investigated due to their low cost versus the platinum-group metals. For this paper, platinum and silver promoted and unpromoted catalysts will be compared.

Experimental

Synthesis of Unpromoted Co/Al₂O₃ FT Catalysts

For catalyst synthesis at GRC, procedures were modified based on a description in a U.S. patent by Espinoza, et al. (Ref. 12). A summarized procedure list can be found in Table I.

TABLE I.—SUMMARY OF TARGET LOADING
OF UNPROMOTED CATALYSTS

Step 1	First Co loading > Rotavap
Step 2	Second Co loading > Rotavap
Step 3	Calcination
Step 4	Characterization

Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) is dissolved in distilled deionized H_2O. The Co solution was then added to a dispenser titration burette and added dropwise to the alumina (Al_2O_3) (Figure 1), stirring constantly for 30 min without heat. The cobalt nitrate/alumina mixture is heated and stirred in a water bath at 80 °C, under vacuum for water extraction via Rotavapor 210 and Vacuum Pump V-700 (BÜCHI Labortechnik) until it is bright pink and powder dry (Figure 2). Repeat the above steps for a second Co impregnation onto the alumina. The catalyst is then removed and prepared for calcination. Calcination is the thermal treatment applied to solid materials to cause a phase transition or removal of any volatiles. In this case, when the catalyst is calcined, the nitrates present are removed through the release of nitric oxide (NO). This calcination furnace is composed of a sealed long 1-in. OD stainless steel tube packed with glass wool. The catalyst is loaded into the reactor with a thermocouple in place to monitor the internal temperature of the material. Air is flowed through the tube at about 5 mL/min to ensure that the volatiles are carried out of the reactor. Additionally, air is used to make certain the catalyst does not burn. The stainless steel tube is placed into a Blue M tube furnace (Thermo Scientific Lindberg/Blue). Then, the cobalt nitrate/alumina powder is heated to an internal temperature of 350 °C for 4 hr where the temperature is programmed and controlled by the CN3251 Controller Box (Omega). The catalyst is then characterized with SEM/EDS, BET, and TPR.

Synthesis of Promoted Co/Al₂O₃ FT Catalysts

Promoted FT catalysts are prepared by adding promoter salt solutions to an uncalcined, unpromoted Co/Al_2O_3 catalyst, in this case $[Pt(NH_3)_4][NO_3]_2$ or $Ag(NO_3)$. Target loadings of

promoters are usually between 0.5 and 1 percent of the catalyst mass, however up to 2 percent and even 5 percent have been used. The promoter solution is then added dropwise to the unpromoted catalyst, stirring constantly for 15 min without heat. The catalyst is then placed on the Rotavapor where it is heated in a 70 °C water bath. At this stage, the catalyst is pink and powder dry; it is placed in the calcination reactor where it is calcined using the unpromoted catalyst specifications. The finished catalyst is a fine black powder, shown in Figure 3. It should be noted that more than one promoter can be added to catalyst. One would simply repeat Step 3 before calcination is completed. A summary of the promoter addition procedure is given in Table II.

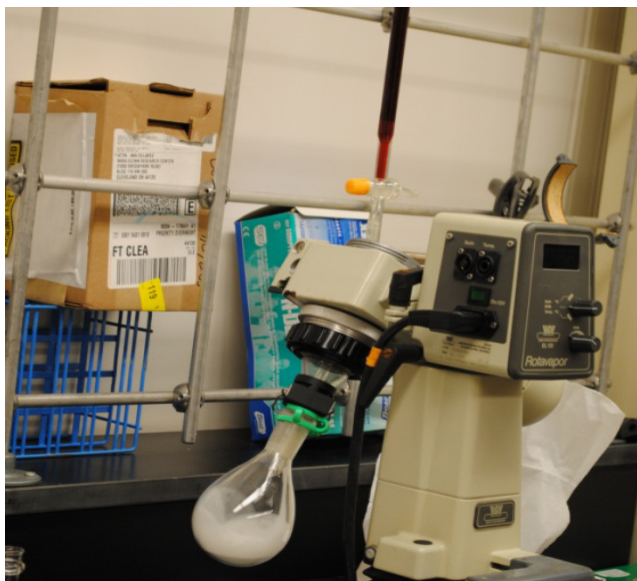Figure 2.—Catalyst drying before calcination on Rotavapor 210.

Figure 1.—Impregnation of Co on alumnia dropwise from burette.

Figure 3.—Completed catalyst after calcination. Promoted and unpromoted catalysts both are black powders upon completion.

TABLE II.—SUMMARY OF TARGET LOADING
OF PROMOTED CATALYSTS

Steps 1 and 2	First Co loading > Rotavap > Second Co loading > Rotavap
Step 3	Promoter loading > Rotavap
Step 4	Calcine
Step 5	Characterization

Catalyst Characterization Methods

For FT synthesis, there are many factors that may affect the overall selectivity and conversion of CO during the reaction and also the type of hydrocarbon product produced. The goal of FT synthesis research at GRC is to develop a heterogeneous catalyst that can generate a specific type or range of hydrocarbons needed for an application (terrestrial transportation, aviation, etc.). When characterizing catalysts, the goal is to understand the surface of the catalyst at the microscopic and mesoscopic level at reaction specific conditions (Ref. 13). These studies would include analysis of the catalytic activity per unit area, the catalyst behavior based on the composition of the material, surface adsorption, and electron microscopy (Ref. 3).

Energy Dispersive Spectroscopy and Scanning Electron Microscopy

Energy dispersive spectroscopy (EDS), based on x-ray florescence spectroscopy, is used to determine specific surface properties and elemental composition of a given material on the sub-micron scale (Ref. 14). As samples are excited with electrons in an electromagnetic field, x-rays are emitted. Since each element has a different atomic structure, the x-ray emitted can be identified and the element can be determined. X-ray florescence occurs when the vacated shell is filled with an electron from a higher shell. The energy gain by a specific signature or pattern from this transition is used to emit an x-ray photon, which is unique to that atom. EDS also competes with internal photoionization. Thus, the probability is the highest for elements heavier than magnesium (Ref. 13). Emitted x-rays are analyzed by an energy dispersive x-ray detector that is located at a fixed point about the sample. The detector converts the photon, via the photoelectric effect, into an electron where the current is measured. The pulse height is then recorded (Refs. 13 and 14).

Scanning electron microscopy (SEM), in conjunction with EDS, allows the observation and *in situ* chemical analysis of heterogeneous materials at the micron level. There is a very wide range of magnification available on most SEM microscopes. A material can be analyzed at magnifications as low as 10X to as high as 500,000X for some models (Ref. 15). The instrument ordinarily operates at low vacuum pressures to permit the use of electron beams on the surface of the materials that are undergoing analysis (Ref. 15). A narrow electron beam in a raster scan pattern is produced over the surface of the material and backscattered; secondary electrons are produced by the primary beam and are used as the primary signals to form images. The contrast of the images is based on the orientation of the surface of the material to the detector (typically using EDS technology) (Ref. 13). Bright sections of the material have the surface normal facing the detector, whereas the dark sections have the surface normal pointing away. The backscattered electrons carry information about the composition of the sample, since these electrons increase with an increase in atomic weight of the material (Ref. 14). Since, higher atomic weight elements are more efficient at scattering electrons throughout an area, these elements will appear brighter in SEM images (Ref. 16). Because such a narrow electron beam is used, SEM yields a three-dimensional analysis of the surface of the material which is very useful for structural analysis.

Temperature Programmed Reduction

Temperature-programmed studies involve assessments in which a chemical reaction is analyzed as the temperature is raised at a linear rate (Ref. 17). A TPR instrument consists of temperature programmable equipment and a thermal conductivity detector (TCD) and is loaded with a catalyst in a sample tube. To remove the oxygen from the sample, an inert gas (usually He or Ar) is flowed through the catalyst until the TCD signal is constant. The instrument heats the sample as the temperature is increased at a rate of 1 to 20 °C/min. During this increase in temperature, the TCD measures the amount of H_2 in the gas entering and leaving the instrument. For a typical TPR, one would use 4 to 10 percent H_2 in N_2 in Ar. When reduction occurs, H_2 is consumed, which in turn increases the signal on the detector (Ref. 18). Total amount of H_2 consumed can also be determined via the amount of water produced during the reaction. When a substance is reduced, the Gibbs free energy (by convection) is negative; the reaction is thermodynamically favorable and will release energy (exothermic) (Ref. 19). Because the product of the FT catalyst reduction by hydrogen is water, and the free enthalpy is always negative (by $\Delta G = \Delta H - T\Delta S$). From the TCD signal versus temperature plot, one can easily find the reduction/activation temperatures from peaks on the graph. If the catalyst contained multiple metals (i.e., a promoted catalyst), the plot should contain multiple peaks where the additional metals were reduced. This information can then be used to determine the multiple phases of the catalyst after the Co and promoter impregnation and can indicate the arrangement of the metals on the surface of the alumina support. Additionally, the reduction temperature is used to

verify the activation energies and activation temperatures to be used in the FT reactors. At GRC, TPR is performed and analyzed on the AutoChem II 2920 (Micromeritics Instrumentation Corporation).

Brunauer, Emmett, and Teller Surface Area Analysis

Since catalysis in FT and many other reactions occur on the surface, the area available on the material available for reaction(s) is vital information for characterizing catalysts and the outcomes of FT synthesis, in particular. The Brunauer, Emmett, and Teller (BET) method is used to determine the surface area and is based on physisorption: the amount of gas that can physically adsorb onto a surface at a given pressure. The physisorption of a material is based on the interactions between the surface of the catalyst with the gas vapor pressure and the temperature. Because BET is very inexpensive and reliable, it is used in many research areas where the surface area of a material is needed. However, the test does not apply to all types of isotherms (Ref. 13).

In catalysis research, the surface area of the catalyst is very important with regards to the activity and stability of the material. The original BET theory is based on the original surface area of the Langmuir isotherm. Major advancements in adsorption models used the Langmuir isotherm, which described the accumulation of gas molecules in a monolayer on a surface to illustrate multilayer adsorption (Ref. 20). The supporting statements in BET theory state that the forces present in the condensation of gases are responsible for the multilayer binding on the surface of the catalyst. For an infinite number of layers, the BET characteristic equation can be found by summing the rate of condensation of gases onto an adsorbed layer and the rate of evaporation of the monolayer already of the surface (Ref. 18):

$$\frac{P}{V_a(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left[\frac{P}{P_0}\right]\dots \qquad (3)$$

In Equation (3), P_0 and P are the saturation and equilibrium pressures of adsorbed gases at the temperature of adsorption. V_a is quantity of adsorbed gas in units of volume and V_m is quantity of gas in the adsorbed monolayer. C is the BET constant, which is incorporates the heat of liquefaction of the monolayer and subsequent adsorbed gas layers on the surface. Equation (3) describes the equilibrium of the adsorption of gas on the catalyst surface at a constant temperature, and can be plotted in a linear relationship.

The BET multilayer adsorption model is based on a series of assumptions. Firstly, as stated above, it is assumed that the gas molecules can adsorb onto the surface of catalyst in infinite layers. Second, there are no interactions between the gas layers; and third, the monolayer model applies to each individual layer (Ref. 20).

The most common procedure to measure the surface area of a catalyst is to observe how much N_2 is adsorbed onto the material at low pressure and temperature (Ref. 21). The NASA catalyst synthesis group uses a FlowSorb III 2305 (Micromeritics Instrumentation Corporation) for BET analysis. This instrument has the capability of reporting adsorption and desorption isotherms. A catalyst (or catalyst material, such as the alumina support) is loaded in a sample tube. A heating mantle is installed to raise the temperature of the sample to about 250 to 300 °C while the catalyst is exposed to flowing N_2 to purge any air or water in the sample or tube. After degassing, the catalyst is prepared for analysis. A TCD is used to measure the thermal conductivity at the start of the experiment. Since the sample will not adsorb nitrogen at room temperature, the sample tube is immersed in a Dewar flask of liquid nitrogen (LN_2). The sample almost immediately begins to adsorb nitrogen onto the surface. As the nitrogen molecules begin to adsorb on the surface, the thermal conductivity also changes. After the maximum amount of N_2 is adsorbed, the Dewar is removed to investigate the desorption of the catalyst (Ref. 21). Since the same amount of nitrogen should be adsorbed and desorbed, these values should be very close in values. The amount of nitrogen consumed is then used to determine the surface area of the catalyst in m^2/g, based on the weight of the sample loaded in the instrument.

Methods

TPR Procedure

As stated previously, for TPR analysis was performed via an AutoChem II 2920 (Micromeritics Instrumentation Corporation). A sample, 0.1 to 0.2g by weight, is loaded into a quartz U-tube packed with glass wool at the bottom to hold the catalyst in place. The tube, with a thermocouple in place to measure the internal temperature of the catalyst, is then secured in the furnace vessel of the instrument. Argon is subsequently flowed through the instrument to remove any excess oxygen in the catalyst and to also stabilize the TCD before analyzing the sample. An ice-salt bath, at a temperature of –5 °C was installed at the cold trap of the instrument. The temperature is then ramped to 1000 °C at a rate of 10 °C/min while flow controllers inject 4 percent H_2/Ar at a rate of 30 cm^3/min. The TCD signal is recorded as a function of the temperature ramp throughout the analysis to determine the multiple activation temperatures of the catalyst. The TPR unit used for catalysis investigations is pictured in Figure 4.

SEM/EDS Procedure

FT catalysts were analyzed using S-3000N scanning electron microscope (Hitachi) for imaging and energy dispersive spectroscopy to determine the elemental composition and the surface properties of the material. The samples were prepared by placing some of the catalyst powder onto a strip of copper tape. Before the high vacuum mode is initiated, the strip is then inserted onto a sample holder and inserted into

Figure 4.—Micromeritics AutoChem II 2920 used for TPR analysis.

Figure 5.—Micromeritics FlowSorb II 2300 used for BET analysis.

the specimen stage of the SEM. The electron images were viewed at 16.0 and 25.0 keV and at magnifications of 200X and 250X. The working distances of the microscope varied, usually between 15 to 25 mm. Elemental composition data was attained using SEM Quant ZAF microanalysis software with a silicon drift detector used for EDS via the EDAX detecting unit (AMETEK).

BET Procedure

The FlowSorb II 2300 (Micromeritics Instrumentation Corporation), pictured in Figure 5, was used to obtain surface area measurements of the catalysts. Approximately 0.2g of catalyst is measured into an empty glass U-tube. It is imperative that the exact weight of the material is noted, since this value is crucial to the accuracy of the surface area measurement. The sample tube is inserted into the sample tube holder and secured by tightening connectors that seal via compressed O-rings, making a closed system assembly.

The catalyst must be degassed before it can be analyzed for surface area in order to remove any water vapor or other gases present during normal exposure to air. To achieve this, sample tube is attached to the degas section of the instrument via quick connect locking mechanisms. The sample is the heated via a heating mantle to a temperature of 250 °C for approximately 30 min while 30 percent N_2/He is flowed. Once the catalyst is completely degassed, it is allowed to cool for 20 min in the degas area in order to reduce the likelihood of thermal cracking. The sample is then moved to the test position to be prepared for analysis. It should be noted that 30 percent N_2/He is used exclusively for this entire experiment. To trigger the adsorption of nitrogen, a Dewar flask with liquid nitrogen (LN_2) is installed on the sample tube

at the test position. This temperature and pressure change initiates this consumption of N_2. This volume of nitrogen gas adsorbed onto Co/Al_2O_3 was used to find the amount of gas needed to form a single layer of N_2 molecules over the surface. Once adsorption is complete, the Dewar of LN_2 is removed. This removal changes the pressure again, triggering the desorption of nitrogen on the surface of the catalyst. The instrument will then display the surface area of the material. The sample tube is allowed to return to room temperature and the mass is recorded again for precision purposes. To determine the specific surface area in square meters, the displayed desorption reading is divided by the mass of the catalyst sample.

Results and Discussion

Over 50 various heterogeneous FT catalysts have been synthesized and characterized at GRC. An analysis of the chemical composition and morphology were performed via BET, SEM and EDS. Many of the catalysts were sent off-site to Galbraith Laboratories, Inc., for inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analysis to be compared with in-house EDS weight percent data. The weight percents of the promoters and cobalt are of primary interest in this study, since these metals affect the reduction temperatures of the catalysts to the greatest degree. A complete listing of all relevant characterization data found during this inquiry is found in Table III.

TABLE III.—SAMPLES OF PROMOTED/UNPROMOTED Co/ALUMINA CATALYTS PREPARED AT GRC

Sample no.	Promoter	ICP-AES element analysis	EDS	Surface area (m^2/g)	Reduction temperature (°C)
1	None	21.6% Co/Al_2O_3	30.3% Co/Al_2O_3	126.3	350
2	None	9.31% Co/Al_2O_3	9.45% Co/Al_2O_3	142.4	335
3	None	31.7% Co/Al_2O_3	47.2% Co/Al_2O_3	108.7	436
4	Pt	21.5% $Co/0.845\% Pt/Al_2O_3$	25.4% $Co/2.57\% Pt/Al_2O_3$	123.7	254
5	Pt	20.9% $Co/0.397\% Pt/Al_2O_3$	24.1% $Co/1.49\% Pt/Al_2O_3$	106.6	349
6	Pt	24.8% $Co/0.459\% Pt/Al_2O_3$	34.8% $Co/2.30\% Pt/Al_2O_3$	115.9	265
7	Ag	21.0% $Co/0.806\% Ag/Al_2O_3$	25.9% $Co/1.31\% Ag/Al_2O_3$	118.2	275
8	Ag	23.6% $Co/0.278\% Ag/Al_2O_3$	33.3% $Co/2.19\% Ag/Al_2O_3$	109.4	369
9	Ag	22.9% $Co/0.510\% Ag/Al_2O_3$	26.7% $Co/1.63\% Ag/Al_2O_3$	117.6	337

When performing elemental analysis, it is important to understand that the amount of cobalt reported is representative of the amount of cobalt that has been distributed on the alumina, confirming a successful synthesis of a FT catalyst. When a promoter is added, the usual target loading is between 0.1 and 0.5 percent of the total mass of the catalyst. Reported values from Galbraith were within 15 percent of the targeted initial loading. In this paper, ICP elemental analysis data will be used over EDS testing, since ICP is much more reliable, available, and accurate than that of EDS. Additionally, it should be noted that EDS detected other components in the catalyst that were not in the experimental design. These materials are most likely impurities in the support or chemical similarities of the components during characterization. These impurities are removed for the total weight percent of the metals in the sample. Since the platinum loading was very low, it was not detected during EDS analysis.

The SEM images below are typical of the catalyst materials synthesized during this study. From Figure 6 and Figure 7, the surfaces look smooth and spherical particles look evenly dispersed throughout the alumina support. This smooth surface is desirable, since it reduces the surface area and provides a better plane for FT synthesis to occur. Figure 6 was viewed at working distance of 22.9 mm and at magnification of 250X. Figure 7 was recorded at a working distance of 15.0 mm and at a magnification of 200X.

For unpromoted catalysts, the specific surface area of the catalysts generally decreases as the percent of cobalt increases. The starting surface area for the alumina support was 200 m^2/g (reported by Sasol, Inc.). With the addition of cobalt onto the support to create the FT catalysts, the surface area decreases with increased cobalt metal. This is aptly demonstrated by catalyst no. 3, which had an increase to 31 percent Co loaded on the alumina. The surface area dropped notably from 142.4 to 108.7 m^2/g upon tripling the cobalt loading. Additional unpromoted catalysts would need to be investigated to provide a quantitative relationship. The promoted catalysts were also evaluated according to their corresponding surface areas. As depicted in Figure 8, there is a clear downward trend with regards to the weight percent
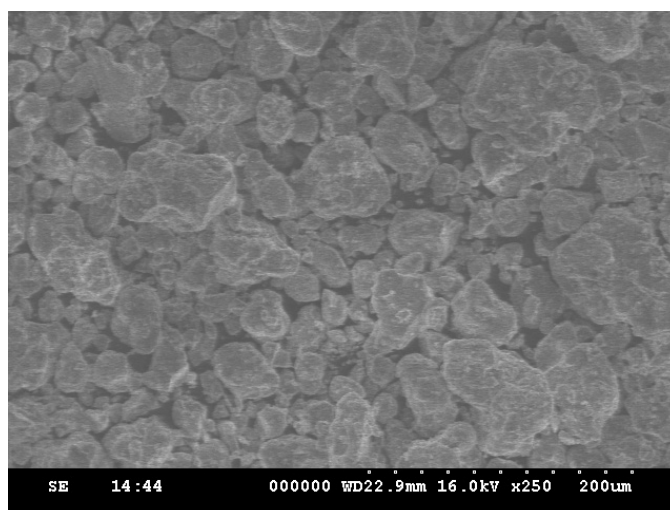

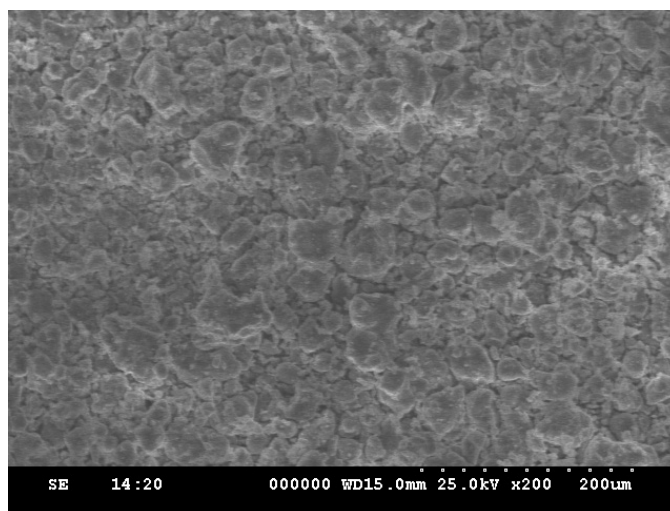Figure 6.—SEM image of 21.6 percent Co/Al_2O_3 catalyst at 250X magnification.

Figure 7.—SEM image of 21.5 percent $Co/0.845$ percent Pt/ Al_2O_3 catalyst at 200X magnification.
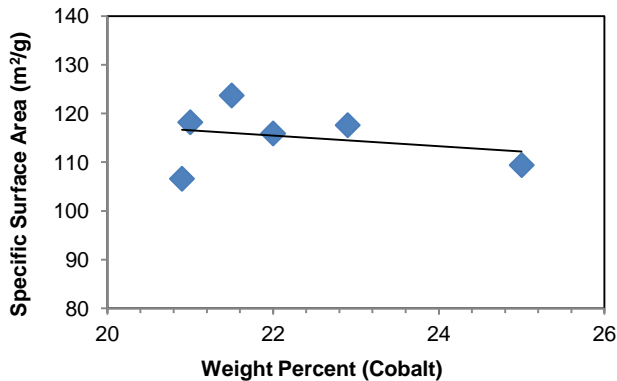
Figure 8.—Percentage of cobalt versus specific surface area of promoted catalysts.
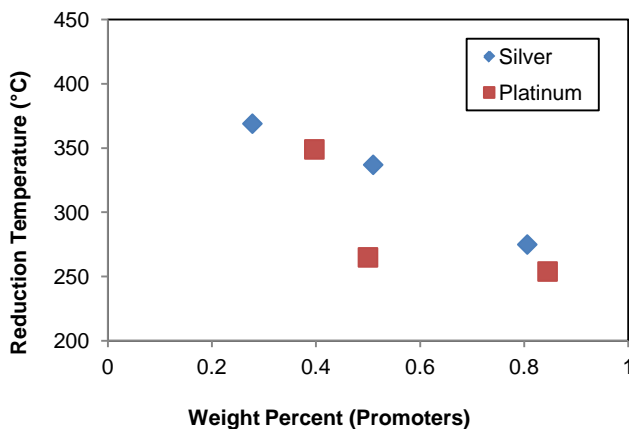

Figure 9.—Promoter weight percent versus the reduction temperatures of Pt and Ag promoted FT catalysts (with trendlines)

of cobalt and the specific surface areas of the promoted catalysts. This result, furthermore, agrees with the conclusion above affirming that the addition of supplementary cobalt and promoters to the FT alumina support decreases the surface area. Additionally, the weight percent of the promoters was analyzed. It was expected that that with the higher amount of promoter present, the specific surface area will be higher because the metal promoter is not occupying the porous space. Rather, the promoter attaches to the surface. Unlike cobalt, the specific surface area is inversely proportional to the percent loaded. For both platinum and silver, the surface areas of the FT catalysts increased as the amount of promoter loaded increased. The most plausible explanation for this phenomenon most likely involves the surface attachment of the particles on the surface of the alumina. Since the cobalt fills the majority of the porous spaces of the support, usually the promoter is given little space to fill inside the alumina, thus increasing the surface area of the catalyst.

In addition to BET, TPR was performed on all catalysts above to determine the corresponding reduction temperatures. In theory, the addition of promoters to an FT catalyst should reduce the reduction temperature, and therefore operation temperature, of FT synthesis. As seen from Table III, the reduction temperature of an unpromoted catalyst varies from 350 to 425°C. Ideally, the aim is to reduce the temperature needed for activation and operation. However, the addition of promoters drastically reduces this temperature. The trends between promoter weight percent and reduction temperature is shown in Figure 9. For both silver and platinum, as the weight percent of the promoter loaded is increased, the temperature is then decreased. Platinum seems to have a greater effect on the reduction, than that of its' silver counterpart. Even with the addition of 0.3 percent of silver on the catalyst, the reduction temperature remains at 369 °C. The amount of silver needed must be increased close to 1 percent for any great effect to occur. However, platinum reduces at a lower temperature with the addition of only 0.5 percent of the catalyst weight. From the figure, it can be concluded that platinum promoted catalysts cause the reduction temperature to decrease a much faster rate than that of silver with smaller amounts of noble metal.

Conclusion

Through this research, GRC's Alternative Fuels group is steps closer to finding novel aviation fuel range catalysts for use in the FT synthesis process. The data presented verifies that that production of promoted and unpromoted Co/Al_2O_3 is feasible at relatively mild reaction conditions. Our preliminary results are in accord with prior literature (Ref. 22); the available surface area of a heterogeneous material will impact catalytic activity simply by altering the number of active sites. The specific activity of a catalyst also depends upon the metal(s) and dispersion onto the support.

In summary, initial results suggest that upon increase of cobalt on the alumina, the specific surface area of the catalyst decreases. This result coincides with other observations made in previous FT catalyst research. Moreover, since the specific surface area of the Co/Al_2O_3 was reduced, a smoother surface was created. However, this inclination is not the same for platinum and silver loadings, due to the surface attachment of the promoter onto the exterior of the support. Additionally, through TPR investigation, it was observed that promoting Co/Al_2O_3 with platinum reduced the reduction temperature to the greatest extent. Since the main goal behind promoting catalysts is to reduce the activation temperature of the catalyst, platinum and chemically-similar metals would be obvious candidate promoters for future catalysis investigations.

Future work involves the investigation of varying Co/Al_2O_3 loading and use of other promoters from the platinum-group and coinage metals to determine the impact on reactivity and product specificity through TPR and pulse re-oxidation techniques. Additionally, other catalyst supports (TiO_2, SiO_2, and doped-Al_2O_3) will be investigated to determine the ideal

porosity of the material for FT synthesis. This data will then be collected to continue research into catalysts that specifically target aviation fuel production via FT synthesis.

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14. ABSTRACT
Due to environmental, economic, and security issues, there is a greater need for cleaner alternative fuels. There will undoubtedly be a shift from crude oil to non-petroleum sources as a feedstock for aviation (and other transportation) fuels. Additionally, efforts are concentrated on reducing costs coupled with fuel production from non-conventional sources. One solution to this issue is Fischer-Tropsch gas-to-liquid technology. Fischer-Tropsch processing of synthesis gas (CO/H_2) produces a complex product stream of paraffins, olefins, and oxygenated compounds such as alcohols and aldehydes. The Fisher-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur or aromatic compounds. This process is most commonly catalyzed by heterogeneous (in this case, silver and platinum) catalysts composed of cobalt supported on alumina or unsupported alloyed iron powders. Physisorption, chemisorptions, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) are described to better understand the potential performance of Fischer-Tropsch cobalt on alumina catalysts promoted with silver and platinum. The overall goal is to preferentially produce C8 to C18 paraffin compounds for use as aerospace fuels. Progress towards this goal will eventually be updated and achieved by a more thorough understanding of the characterization of catalyst materials. This work was supported by NASA's Subsonic Fixed Wing and In-situ Resource Utilization projects.

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